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Kinetics of the Reactions of F⁻ with CF₃Br and CF₃I as a Function of Temperature, Kinetic Energy, Internal Temperature, and Pressure

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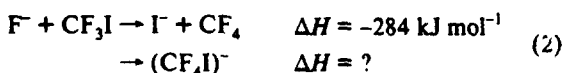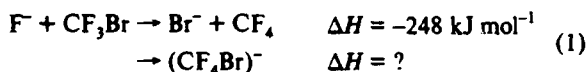*Received: October 6, 1993; In Final Form: December 3, 1993*®

The reactions of F⁻ with CF₃Br and CF₃I have been studied at several temperatures as functions of pressure and ion-neutral average center-of-mass kinetic energy ($\langle KE_{cm} \rangle$). Rate constants and product branching fractions were measured by using a variable temperature-selected ion flow drift tube apparatus. Both title reactions involve two product pathways: displacement and association, the latter being the major channel under most experimental conditions. The rate constants for displacement are governed by total energy, regardless of the relative contributions by translational and internal energy, indicating that the displacement reactions behave statistically. In contrast, the rate constants for association depend strongly on the internal energy of CF₃X (rotations and vibrations) compared with the relatively weak effect of translational collision energy. For CF₃Br the rate constants for the association channel increase with increasing pressure while those for displacement are independent of pressure, indicating that the additional reactivity leading to more association at higher pressure appears not to compete with the displacement pathway. This lack of competition may be the result of two different reaction intermediates. The more efficient CF₃I reaction is at or near the high-pressure limit for association, showing no pressure dependence in both the association and displacement channels. Therefore, there appears to be no competition between these channels for CF₃I as well, but the data are less definitive in this case.

Introduction

Gas-phase nucleophilic displacement reactions have become the focus of a great deal of research in recent years. Much of the interest centers on the dynamics of such reactions and, in particular, on whether these reactions can be described by statistical theories. Recent experimental and theoretical work has indicated nonstatistical behavior in certain displacement reactions.[1-11]

For systems in which multiple reaction pathways exist, it is also interesting to examine whether these channels compete with one another or are uncoupled. In some cases, multiple pathways have been shown to be competitive;[12-14] that is, a change in experimental conditions, e.g., pressure, which favors a particular channel will lead to a corresponding decrease in another channel. In other cases, no tradeoff between pathways is seen.[15]

In the present work, the reactions of F⁻ with CF₃Br and CF₃I were studied in order to (1) examine whether the reactions behave statistically and (2) examine the possibility of competition between displacement and association by studying the rate constants for the individual channels as a function of pressure. These reactions were chosen partly because a recent survey of halocarbon reactions[16] from our laboratory showed that both displacement and association are significant pathways. Association dominates the reactivity for both reactions under room temperature conditions, despite the fact that bimolecular displacement of Br⁻ or I⁻ is highly exothermic.[17]

$$F⁻ + CF_3Br \rightarrow Br⁻ + CF_4 \qquad \Delta H = -248 \text{ kJ mol}^{-1}$$
$$\rightarrow (CF_4Br)⁻ \qquad \Delta H = ? \qquad (1)$$

$$F⁻ + CF_3I \rightarrow I⁻ + CF_4 \qquad \Delta H = -284 \text{ kJ mol}^{-1}$$
$$\rightarrow (CF_4I)⁻ \qquad \Delta H = ? \qquad (2)$$

In order to learn whether the displacement component of the reaction behaves statistically, i.e., whether statistical theories can

adequately describe the reactivity, we have examined the role of internal temperature in influencing reactivity and product branching using a technique developed in this laboratory.[18] For the displacement reaction to behave statistically, the influence of internal energy on the rate constant must be the same as that of translational energy, i.e., total energy must govern the reactivity irrespective of the relative contributions from internal and translational energy.[9] Measurements made as a function of ion kinetic energy at each of several temperatures yield information about dependences on the internal temperature of the reactants and give the translational energy dependence. In the present case, where the ionic reactant F⁻ is monatomic, the derived internal temperature dependence pertains to the internal temperature of the CF₃X reactant neutral.

In this article we report rate constants and product branching fractions for the reactions of F⁻ with CF₃Br and CF₃I under a wide range of experimental conditions. At each of several temperatures, the kinetic parameters (rate constant and branching fractions) were measured as functions of both pressure and ion kinetic energy. The kinetic energy dependences were measured while maintaining the total He buffer gas number density at a constant value at all temperatures. This allows for a more straightforward comparison of the data obtained under different conditions. Thus, for each reaction, the experiments yield a pure temperature dependence, kinetic energy dependences at each temperature, and pressure dependences at each temperature. Furthermore, the dependence on the internal temperature of CF₃X is derived.

Experimental Section

The experiments were performed using a variable temperature-selected ion flow drift tube (VT-SIFDT) instrument. The technique has been fully described in the literature.[19] The following is a brief description of the details specific to the present study. F⁻ ions were generated by electron impact on SF₆ in a high-pressure (0.1–1 Torr) ion source. The ions were then mass selected in a quadrupole mass spectrometer and injected into a stainless steel flow tube 1 m in length through a Venturi inlet.

Inside the flow tube the ions were entrained in the fast flow ($\sim 10^4$ cm/s) of He carrier gas which flows from the Venturi inlet. The CF_3Br or CF_3I reactant neutral was introduced into the flow tube through one of two ring-shaped inlets and reacted with the ions over distances of 50.3 or 35.4 cm depending on which inlet was used. The reactant and product ions were sampled through a 0.2-mm-diameter orifice in a truncated nose cone, mass analyzed in a second quadrupole mass spectrometer and detected by a channel particle multiplier. Rate constants were calculated from the reaction times and the slopes of least-squares fits of the natural logarithm of the reactant ion signal plotted versus added reactant neutral gas concentration. The reaction time was obtained from the reaction distance and from direct ion time-of-flight measurements in the flow tube. The accuracy of the measured overall rate constants is ±25%, and the experimental precision is ±15%. The rate constant for an individual reaction channel is equal to the overall rate constant multiplied by the product branching fraction for that channel. Therefore, the accuracy with which the branching fraction can be measured must be considered, and we estimate the uncertainty in the channel-specific rate constants to be ±35% with a precision of ±20%.

The experiments were conducted over the temperature range 153–525 K by circulating liquid nitrogen through a copper heat exchanger in contact with the flow tube for cooling and by heating the heat exchanger with attached resistive heaters. The rate constants and branching fractions were also measured as a function of ion kinetic energy at the various experimental temperatures by applying a uniform electric drift field inside the flow tube. The average kinetic energy in the ion-neutral center-of-mass frame is denoted $\langle KE_{cm} \rangle$. In the case of the CF_3Br reaction, a rate constant energy dependence could not be measured at 525 K due to the slow reaction rate, low signal levels, and short reaction time with the drift field on. Also, for the same reasons, at 410 K only one "field on" rate constant could be measured, but it was possible to measure the energy dependence of the branching fractions at 410 and 525 K. The desired operating pressure in the flow tube was maintained by a servo-controlled butterfly valve in the flow tube pumping line.

Product ion branching fractions were measured by operating the downstream mass spectrometer at low resolution to avoid mass discrimination. The low-resolution condition leads to good balance between the reactant ion decline and the total product ion increase. For branching fraction determinations, the product ion signals were recorded as a function of reactant neutral flow rate at low extent of reaction. Reported branching fractions are the result of extrapolating the branching fractions to zero reactant neutral flow rate in order to account for secondary reactions in the flow tube. The values reported are averages of several runs. The observed secondary reactions are association reactions of the product ions with the reactant neutral CF_3X.

Internal temperature dependences are obtained by comparing rate constants (or branching fractions) at a particular kinetic energy ($\langle KE_{cm} \rangle$) which were measured at different temperatures. This comparison yields the dependence on the internal temperature of the CF_3X reactant neutral since the F⁻ reactant ion has no internal modes. A detailed description of this technique for deriving internal temperature dependences has been published.[18]

Results

Rate constants for the overall reaction (loss of F⁻) and for the individual reaction channels (displacement and association) and the product branching fractions for these channels are reported in Tables 1–4. The subscripts D and A refer to the displacement and association channels, respectively. Tables 1 and 2 give the kinetic energy ($\langle KE_{cm} \rangle$) dependences at several temperatures, and Tables 3 and 4 give the pressure dependences at several temperatures. The kinetic energy dependences were all measured with [He] = 1.28×10^{16} cm⁻³, regardless of the temperature.

TABLE 1: Rate Constants (cm³ s⁻¹) and Product Branching Fractions for the Reaction of F⁻ with CF₃Br as a Function of Ion–Neutral Average Center-of-Mass Kinetic Energy ($\langle KE_{cm} \rangle$) at Four Temperatures[a]

T (K)	$\langle KE_{cm} \rangle$ (eV)	$k_{overall}$	k_D	k_A	fraction_D	fraction_A
153	0.020	4.30e-10[b]	8.99e-11	3.40e-10	0.21	0.79
	0.059	2.62e-10	5.50e-11	2.07e-10	0.21	0.79
	0.128	1.45e-10	3.39e-11	1.11e-10	0.23	0.77
	0.239	4.08e-11	1.34e-11	2.74e-11	0.33	0.67
298	0.038	9.21e-11	3.33e-11	5.88e-11	0.36	0.64
	0.072	8.06e-11	3.24e-11	4.82e-11	0.40	0.60
	0.114	5.53e-11	2.36e-11	3.17e-11	0.43	0.57
410	0.053	3.67e-11	1.84e-11	1.83e-11	0.50	0.50
	0.074	4.19e-11	2.04e-11	2.15e-11	0.49	0.51
	0.132				0.59	0.41
	0.223				0.66	0.34
	0.345				0.82	0.18
525	0.068	1.41e-11	1.05e-11	3.57e-12	0.75	0.25
	0.095				0.71	0.29
	0.138				0.76	0.24
	0.204				0.82	0.18
	0.275				0.86	0.14
	0.428				0.94	0.06

[a] The subscripts D and A refer to the displacement and association reaction channels. [b] Read as 4.30 × 10⁻¹⁰.

TABLE 2: Rate Constants (cm³ s⁻¹) and Product Branching Fractions for the Reaction of F⁻ with CF₃I as a Function of Ion–Neutral Average Center-of-Mass Kinetic Energy ($\langle KE_{cm} \rangle$) at Three Temperatures[a]

T (K)	$\langle KE_{cm} \rangle$ (eV)	$k_{overall}$	k_D	k_A	fraction_D	fraction_A
200	0.026	1.43e-09[b]	8.29e-11	1.35e-09	0.06	0.94
	0.062	1.24e-09	8.93e-11	1.15e-09	0.07	0.93
	0.106	8.94e-10	5.01e-11	8.44e-10	0.06	0.94
	0.167	5.44e-10	5.22e-11	4.92e-10	0.10	0.90
	0.306	2.68e-10	3.75e-11	2.30e-10	0.14	0.86
	0.445	1.56e-10	4.16e-11	1.14e-10	0.27	0.73
298	0.038	7.22e-10	7.51e-11	6.47e-10	0.10	0.90
	0.074	6.65e-10	6.52e-11	6.00e-10	0.10	0.90
	0.189	2.86e-10	4.40e-11	2.42e-10	0.15	0.85
	0.352	1.21e-10	2.86e-11	9.24e-11	0.24	0.76
525	0.068	1.67e-10	4.64e-11	1.21e-10	0.28	0.72
	0.094	1.44e-10	3.54e-11	1.09e-10	0.25	0.75
	0.127	1.10e-10	3.01e-11	7.99e-11	0.27	0.73
	0.185	8.32e-11	2.56e-11	5.76e-11	0.31	0.69

[a] The subscripts D and A refer to the displacement and association reaction channels. [b] Read as 1.43 × 10⁻⁹.

TABLE 3: Rate Constants (cm³ s⁻¹) and Product Branching Fractions for the Reaction of F⁻ with CF₃Br as a Function of Pressure (Torr) at Four Temperatures[a]

T (K)	pressure	$k_{overall}$	k_D	k_A	fraction_D	fraction_A
153	0.20	4.30e-10[b]	8.99e-11	3.40e-10	0.21	0.79
	0.40	5.22e-10	8.40e-11	4.38e-10	0.16	0.84
	0.60	6.14e-10	8.72e-11	5.27e-10	0.14	0.86
298	0.30	8.54e-11	3.09e-11	5.45e-11	0.36	0.64
	0.40	9.21e-11	3.33e-11	5.88e-11	0.36	0.64
	0.55	1.01e-10	3.37e-11	6.73e-11	0.33	0.67
	0.70	1.08e-10	2.95e-11	7.85e-11	0.27	0.73
410	0.35	3.03e-11	1.68e-11	1.34e-11	0.56	0.44
	0.55	3.67e-11	1.84e-11	1.83e-11	0.50	0.50
	0.70	4.10e-11	2.01e-11	2.09e-11	0.49	0.51
525	0.47	c	c	c	0.74	0.26
	0.56	1.52e-11	1.17e-11	3.48e-12	0.77	0.23
	0.70	1.41e-11	1.05e-11	3.57e-12	0.75	0.25[c]

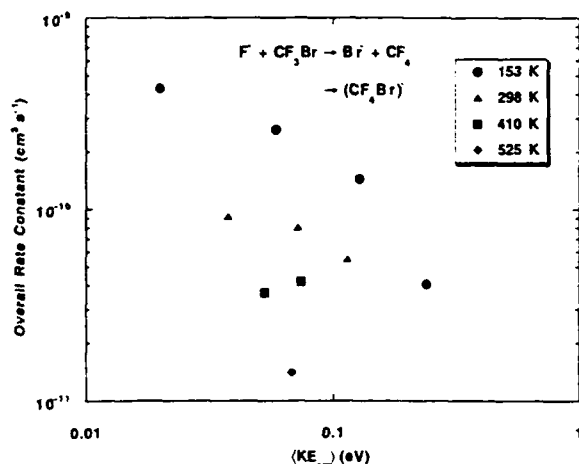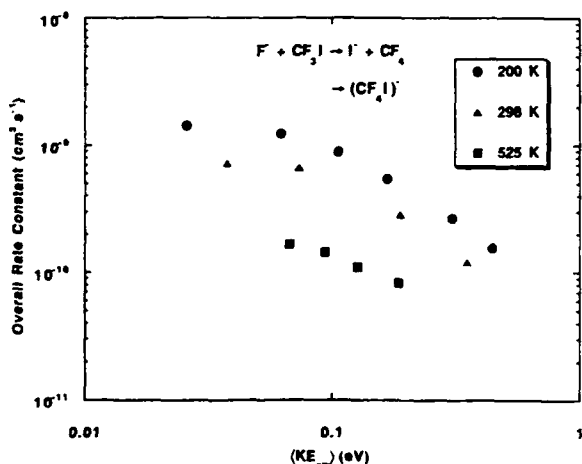[a] The subscripts D and A refer to the displacement and association reaction channels. [b] Read as 4.30 × 10⁻¹⁰. [c] Rate constants not measured reliably at this pressure due to low signal levels.

Figures 1 and 2 show the $\langle KE_{cm} \rangle$ dependences for the overall reactions 1 and 2, respectively. For comparative purposes, Figure 3 shows the $\langle KE_{cm} \rangle$ dependences of the rate constants for both

TABLE 4: Rate Constants (cm^3 s^{-1}) and Product Branching Fractions for the Reaction of F^- with CF_3I as a Function of Pressure (Torr) at Three Temperatures[a]
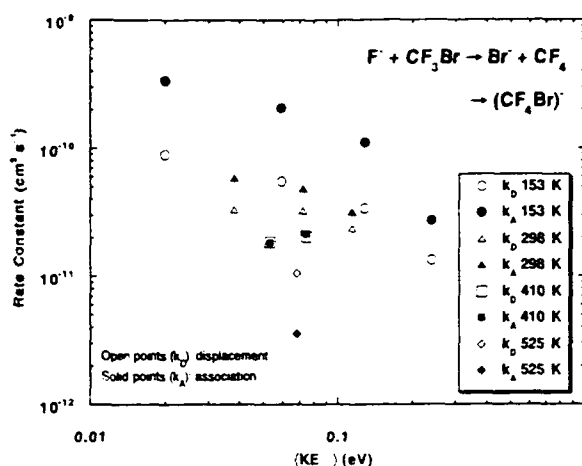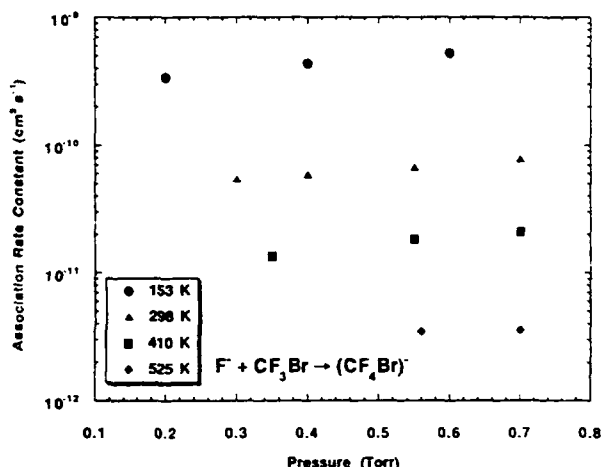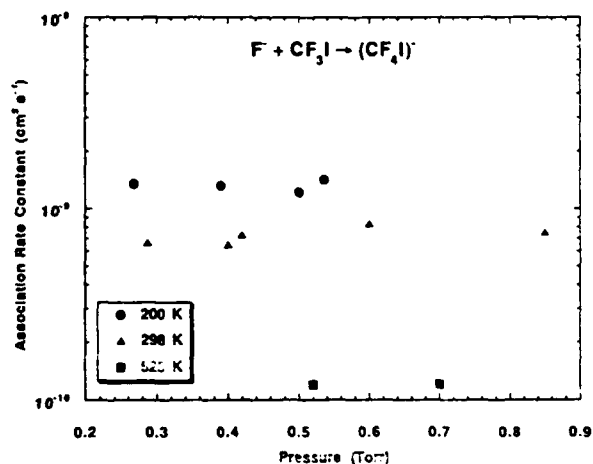
T (K)	pressure	$k_{overall}$	k_D	k_A	fraction$_D$	fraction$_A$
200	0.27	1.43e-09[b]	8.29e-11	1.35e-09	0.06	0.94
	0.39	1.41e-09	8.46e-11	1.32e-09	0.06	0.94
	0.50	1.29e-09	7.35e-11	1.22e-09	0.06	0.94
	0.54	1.49e-09	6.85e-11	1.42e-09	0.05	0.95
298	0.29	7.37e-10	7.08e-11	6.66e-10	0.10	0.90
	0.40	7.22e-10	7.51e-11	6.47e-10	0.10	0.90
	0.60	9.19e-10	8.45e-11	8.34e-10	0.09	0.91
	0.85	8.13e-10	5.69e-11	7.56e-10	0.07	0.93
525	0.52	1.64e-10	4.40e-11	1.20e-10	0.27	0.73
	0.70	1.67e-10	4.64e-11	1.21e-10	0.28	0.72

[a] The subscripts D and A refer to the displacement and association reaction channels. [b] Read as 1.43×10^{-9}.

Figure 1. Rate constants for the overall reaction (displacement and association) of F^- with CF_3Br as a function of $\langle KE_{cm}\rangle$ at several temperatures. Circles, triangles, squares, and diamonds refer to temperatures of 153, 298, 410, and 525 K, respectively.

Figure 2. Rate constants for the overall reaction (displacement and association) of F^- with CF_3I as a function of $\langle KE_{cm}\rangle$ at several temperatures. Circles, triangles, and squares refer to temperatures of 200, 298, and 525 K, respectively.

Figure 3. Rate constants for the individual displacement (open symbols) and association (solid symbols) reactions of F^- with CF_3Br as a function of $\langle KE_{cm}\rangle$ at several temperatures. Circles, triangles, squares, and diamonds refer to temperatures of 153, 298, 410, and 525 K, respectively.

Figure 4. Rate constants for the association reaction of F^- with CF_3Br as a function of pressure at several temperatures. Circles, triangles, squares, and diamonds refer to temperatures of 153, 298, 410, and 525 K, respectively.

Figure 5. Rate constants for the association reaction of F^- with CF_3I as a function of pressure at several temperatures. Circles, triangles, and squares refer to temperatures of 200, 298, and 525 K, respectively.

the displacement and association reactions of CF_3Br on a single graph.

Pressure Dependences. The pressure dependences of the measured kinetic parameters are presented in Tables 3 and 4. Pressure dependences of the association rate constants are shown graphically in Figures 4 and 5 for CF_3Br and CF_3I, respectively, and the rate constants for displacement are shown as a function of pressure in Figure 6 for both CF_3Br and CF_3I. It should be noted for purposes of comparison that the rate constants are plotted

on a 3-decade plot in Figure 4, on a 2-decade plot in Figure 5, and on a 1-decade plot in Figure 6.

The CF_3I reaction is dominated by association and proceeds rapidly, implying that the reaction is at or near the high-pressure limit for association. Furthermore, no pressure dependence was
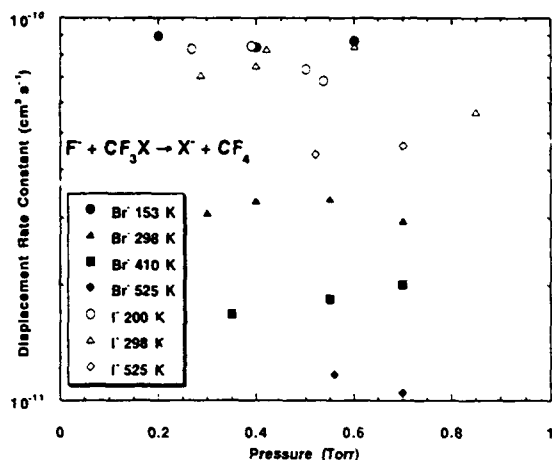
Figure 6. Rate constants for the displacement reactions of F⁻ with CF₃Br (solid symbols) and with CF₃I (open symbols) as a function of pressure at several temperatures.

Figure 7. Rate constants for the association reactions of F⁻ with CF₃Br (circles) and with CF₃I (squares) as a function of temperature. The solid lines are predicted temperature dependences normalized to 298 K (see text).

found in the overall rate constant or in the association channel. For the I⁻ displacement channel, there are slight trends with pressure which are within the experimental uncertainty. The I⁻ displacement rate constants at 200 K have a slight downward trend with increasing pressure, the 298 K data show a slight upward trend, and the 525 K data are flat. This reflects the difficulty of measuring accurately the minor displacement channel in the presence of the efficient association channel. The data do indicate that the I⁻ displacement channel is not largely affected by pressure.

In contrast, the rate constants for association of CF₃Br increase with increasing pressure (Figure 4), but the Br⁻ displacement rate constants are independent of pressure (Figure 6). The pressure dependence of the association channel as shown in Figure 4 may appear to be slight because it is presented on a 3-decade graph, but the rate constant in fact varies by a substantial factor. This can be seen more clearly in Table 3. Also, while the displacement data in Figure 6 may appear more highly scattered than the association data in Figures 4 and 5, this too is largely the result of comparing graphs plotted with different numbers of decades. Thus, the CF₃Br association reaction exhibits low-pressure or falloff behavior, whereas the CF₃I association reaction appears to be at or near the high-pressure limit. These contrasting behaviors with pressure are consistent with the measured temperature dependences of the association rates, discussed in the next section.

Temperature Dependences. The reactions of F⁻ with CF₃Br and CF₃I both exhibit strong negative temperature dependences in the overall rate constants and in the rate constants and branching fractions for association. These features of the association data are not surprising, and since much of the overall reactivity is due to association, the strong negative temperature dependence of the overall rate constant is also expected. The temperature dependences of the association rate constants can be compared with the predictions of low-pressure association theory.[20-22] Figure 7 shows the pure temperature experimental data (no applied electric drift field) for CF₃Br (circles) and CF₃I (squares) as well as the temperature dependence predictions shown as solid lines. The predictions were generated from the expression

$$k_0 \alpha T^{-(l/2)} \prod_i [1 - \exp(-h\nu_i/kT)]$$

where l is the total number of rotational degrees of freedom in the reactants and the product is over all the vibrational frequencies of the reactants.[22] The lines are normalized to the 298 K rate constants and show that the theory predicts the temperature dependence quite well for CF₃Br but not for CF₃I. The disagreement for the CF₃I case is somewhat obscured by the fact

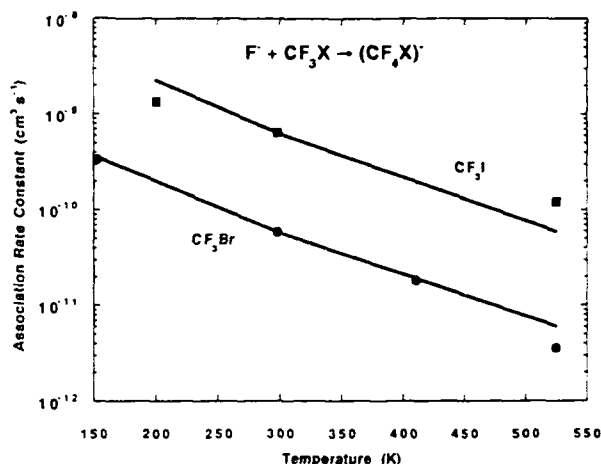that the data are shown on a 4-decade plot, but this disagreement is actually about a factor of 2. Since the lack of pressure dependence of the CF₃I rate indicates that the reaction is at or near the high-pressure limit for association,[23] the disagreement with the low-pressure theory is not surprising. Conversely, the CF₃Br reaction is in or close to the low-pressure limit, and good agreement with low-pressure theory is found. Linear–linear plots of the rate constants for association versus pressure confirm that, above 300 K, the reaction is in the low-pressure regime. At 300 K the reaction begins to show slight falloff behavior, and at 153 K the reaction is clearly in the falloff regime.

Rate constant temperature dependences (and energy dependences) may be expressed as T^n based on the relation $k = CT^n$ where C is a constant. The dependences discussed here derive from least-squares fits of the data points at all temperatures for either the overall reaction or the particular reaction channel of interest. The values of the temperature dependence exponents n are presented mainly for qualitative purposes—to allow trends to be seen more clearly.

The measured rate constants for overall reaction depend on temperature as $T^{-2.7}$ for CF₃Br and as $T^{-2.2}$ for CF₃I. These dependences are dominated by the association component of the temperature dependence; the association rate constants depend on temperature as $T^{-3.5}$ and $T^{-2.5}$ for CF₃Br and CF₃I, respectively. The temperature dependences of the displacement rate constants are weaker at $T^{-1.7}$ and $T^{-0.6}$ for CF₃Br and CF₃I, respectively. The displacement temperature dependences can be compared with those reported previously[6] for the corresponding reactions of F⁻ with methyl halides, for which only displacement is observed in our apparatus. The dependences are $T^{-0.7}$ and $T^{-0.3}$ for CH₃Br and CH₃I, respectively, weaker than those of the corresponding trifluoromethyl halides.

Kinetic Energy Dependences. The overall and channel-specific rate constants for reactions 1 and 2 exhibit mainly moderate negative kinetic energy dependences (weaker than T^{-1}) which are substantially weaker than the pure temperature dependences discussed above (see Figures 1–3).

In the CF₃Br case, the kinetic energy dependences of the overall and channel-specific rate constants appear to vary systematically with temperature, becoming more positive with increasing temperature. This can be seen in Figures 1 and 3. This trend in the overall rate constants is also seen for the association and displacement rate constants.

For CF₃I, both the displacement and association channels display negative dependences on kinetic energy at all three temperatures investigated. Unlike the CF₃Br case, the magnitudes of these dependences do not show a systematic trend with temperature within uncertainty.

Internal Temperature Dependences. As mentioned in the Experimental Section, a comparison of kinetic parameters (rate constants or branching fractions) at a particular $\langle KE_{cm} \rangle$ but at different temperatures yields the dependence of that parameter on the internal temperature of the reactants. Since the monatomic reactant ion F^- has no internal modes, the internal temperature dependence pertains to the internal temperature of the CF_3X reactant neutral. Both CF_3Br and CF_3I have significant populations with vibrational excitation at all experimental temperatures, and these populations change significantly with temperature over the present experimental temperature range. The internal temperature dependence refers to the superposition of rotational and vibrational energy effects.
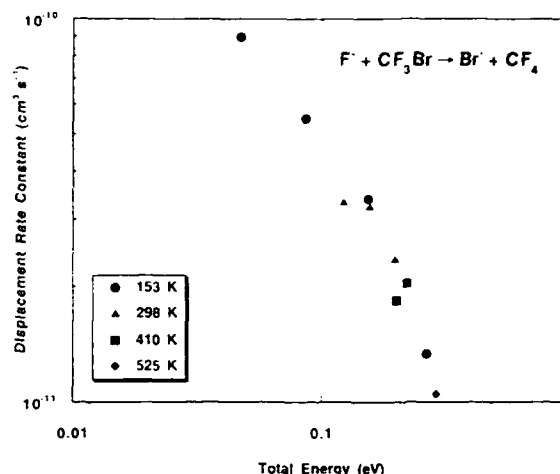
The internal temperature dependence may be viewed by taking a vertical slice through the data points in Figures 1, 2, or 3 and interpolating when necessary. For example, in Figure 1, if one compares rate constants at a $\langle KE_{cm} \rangle$ of 0.068 eV, it is clear that there is a strong dependence on the temperature; the rate constants range from 1.4×10^{-11} cm^3 s^{-1} at 525 K to 2.3×10^{-10} cm^3 s^{-1} at 153 K. This represents a dependence of $T_i^{-2.3}$ for the dependence of the overall rate constant on the internal temperature (T_i) of CF_3Br. (Unlike the pure temperature dependence exponents, which are based on data at all temperatures, the T_i exponents were generated from the pairs of points at lowest and highest temperature.) Values of the internal temperature dependences are given mainly for qualitative purposes of comparison. The internal temperature dependences of the displacement and association rate constants for CF_3Br are $T_i^{-1.3}$ and $T_i^{-3.2}$, respectively, for $\langle KE_{cm} \rangle$ equal to 0.068 eV.

The dependences on the internal temperature of CF_3I are somewhat weaker than those for CF_3Br, most likely due to the greater efficiency of the CF_3I reaction. For the CF_3I reaction, at a $\langle KE_{cm} \rangle$ of 0.068 eV, the overall, displacement, and association internal dependences are $T_i^{-2.0}$, $T_i^{-0.6}$, and $T_i^{-2.3}$, respectively. At a higher $\langle KE_{cm} \rangle$ of 0.185 eV, the values are similar: $T_i^{-1.8}$, $T_i^{-0.4}$, and $T_i^{-2.1}$ for overall reaction, displacement, and association, respectively. The similarity of the internal temperature dependences at different $\langle KE_{cm} \rangle$ values reflects the fact that the $\langle KE_{cm} \rangle$ dependences are not sensitive to temperature.

Discussion

Does Association Compete with Displacement? The pressure dependences of the association and displacement rate constants appear to indicate that these two channels do not compete in the reaction of F^- with CF_3Br under our experimental conditions; i.e., the increase in the association rate constant with increasing pressure is not accompanied by a decrease in the displacement rate constant. This suggests that two different intermediate complexes could be involved in the reaction, one for association and the other for displacement. If this is true, then the data also imply that these intermediates do not interconvert efficiently on the time scale of the experiment. Examples of competing as well as noncompeting channels have been reported previously.[12-15] The noncompetitive nature of the two channels allows an individual channel to be discussed as if the other channel were not present. Since the CF_3I reaction is at or near the high-pressure limit and no pressure dependence was observed in either association or displacement, definitive conclusions about competition cannot be made in this case. However, the fact that, for CF_3I, displacement is unaffected by changes in pressure while the overall reactivity is dominated by association suggests that displacement and association may not compete in this reaction as well.

In the association channel, it is likely that the incoming F^- reactant attacks at the X atom (Br or I) in CF_3X. The positive end of the CF_3X molecule is at the X atom, which is also the more polarizable end, and it is likely that the association product, CF_4X^-, will have the structure $[F_3CXF]^-$ containing a hypervalent halogen atom X. Therefore, the association complex is expected to have

Figure 8. Rate constants for the displacement reaction of F^- with CF_3Br as a function of average total energy at several temperatures. Average total energy is the sum of the average translational, rotational, and vibrational energy of the reactants (see text). Circles, triangles, squares, and diamonds refer to temperatures of 153, 298, 410, and 525 K, respectively.

similar structure. There are numerous examples of hypervalent halogen compounds in the literature, and iodine is more prone to hypervalent bonding than is bromine.[24]

The complex corresponding to displacement may be the classic Walden inversion complex. However, in solution the backside attack or Walden inversion mechanism, which is believed to pei in for displacement reactions of halide ions with monohaloalk .es, is not thought to operate in the case of displacements involving perfluoroalkyl compounds.[25,26] This is attributed to the shielding of carbon by the lone pair electrons on the fluorines. Bimolecular nucleophilic attack at fluorinated carbon has been reported only for the highly strained fluorinated epoxides.[25] While not important in solution, backside attack could be involved in the gas-phase reaction. An alternative is that the displacement channel proceeds via frontside attack at X, as is believed to be the case for association. Our observation that there appear to be two noncompeting complexes in the CF_3Br reaction (and possibly in the CF_3I reaction as well) would seem to favor two distinct complexes and therefore the Walden inversion mechanism.

Energy Effects. In order to find whether the reactivity is governed differently by different types of energy, i.e., translational and internal, or simply by total energy, it is useful to replot the rate constants versus average total energy. Here, we define average total energy as the sum of the average translational, vibrational, and rotational energies of the reactants. If the reactivity is determined solely by the total amount of energy regardless of the type of energy, then one expects the rate constants to lie on a single curve when plotted versus total energy. If the rate constants measured at different temperatures define separate and distinct curves with respect to total energy, then one concludes that internal energy has a different effect on reactivity than does translational energy, per unit energy.

Figure 8 shows the rate constants for displacement in the CF_3-Br reaction as a function of average total energy. Here the data define a single curve, and one concludes that total energy, regardless of the relative contributions from translational and internal energy, governs the reactivity in this case.

In contrast to the displacement channel, the overall and association rate constants for CF_3Br define distinct curves as a function of average total energy at different temperatures and therefore do not depend only on total energy. Figure 9 shows the association rate constants in the CF_3Br reaction as a function of average total energy. The rate constants measured at higher temperature are smaller than those obtained at lower temperature at a fixed average total energy. This indicates that internal energy
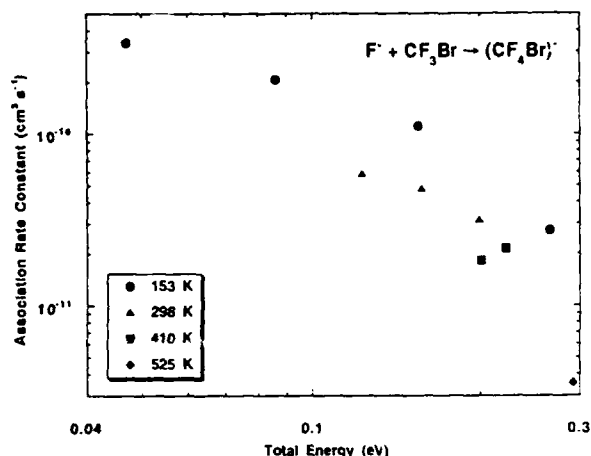
Figure 9. Rate constants for the association reaction of F- with CF₃Br as a function of average total energy at several temperatures. Average total energy is the sum of the average translational, rotational, and vibrational energy of the reactants (see text). Circles, triangles, squares, and diamonds refer to temperature of 153, 298, 410, and 525 K, respectively.

decreases the rate constants for association more rapidly than does translational energy. This is reflected in the fact that increasing internal energy has the relatively strong effect ($T_i^{-3.2}$) of reducing the association rate constant compared with the effect of translational energy ($\langle KE_{cm}\rangle^{-0.5}$ at 298 K).

Similar behavior is seen for CF₃I in that displacement is governed by total energy, although the scatter is greater due to the minor nature of this channel which may obscure a small effect. As in the CF₃Br case, association is also influenced more strongly by internal ($T_i^{-2.3}$) than by translational ($\langle KE_{cm}\rangle^{-0.9}$ at 298 K) energy for CF₃I.

Theoretical understanding of association reactions[20-22] predicts strong effects due to internal energy and relatively weak effects from translational energy, as observed. In the low-pressure regime, the temperature/energy dependence is given essentially by the rotational and vibrational partition function.[22] The CF₃I data do not correspond to the low-pressure regime, so our discussion will concentrate on the CF₃Br data. As seen in Figure 7 the temperature dependence predicted by low-pressure association theory[20-22] fits the data reasonably well for the CF₃Br data even though some of the data pertain to the falloff region. The predicted temperature dependence due to rotations is $T^{-1.5}$. Even at low temperatures, the observed temperature dependence is $T^{-2.7}$, considerably higher than that predicted for rotations only. The good agreement between theory and experiment indicates that vibrational excitation contributes approximately $T^{-1.2}$ to the temperature dependence between 153 and 298 K: 16% of the molecules are in $v > 0$ levels at 153 K while 60% are in $v > 0$ at 298 K. At higher temperatures, the dependence is even steeper, $T^{-3.5}$ between 298 and 410 K and $T^{-6.6}$ between 410 and 525 K. The former value is also in good agreement with theory, while the latter value represents a steeper dependence than that predicted by theory, possibly because the displacement channel becomes the major channel at high temperature. The temperature dependence arises mainly from effects on the lifetime of the complex, and therefore the data clearly show the importance of both rotations and vibrations in determining the complex lifetime.

Statistical Nature of S_N2 Reactions. The question of whether gas-phase ion–molecule S_N2 reactions behave statistically has recently been the subject of a number of studies.[1-11] For reactions that behave statistically, the rate constant depends on the total energy and total angular momentum.[23] Aside from the angular momentum constraint, differing types of energy influence reactivity equally. Therefore, a simple test of the statistical nature of a reaction is to measure kinetic energy dependences at several

temperatures and plot the rate constants versus average total energy. For reactions that behave statistically, all the data should fall on a single curve. This assumes that the angular momentum of the reactant neutral does not influence the reactivity significantly. We have studied the influence of rotational energy on a number of reactions and found that, in most cases, rotational energy does not strongly affect reactivity.[6,18,27-42] In those cases where it does, there are special circumstances: the reaction is either endothermic[31] or is affected to a large degree by charge–dipole locking because of a large neutral dipole moment and rotational constant.[18] The present reactions do not fit into these categories, and no other effect is expected which would involve a large influence from rotational energy. Therefore the total energy test is expected to be valid.

As discussed above, the total energy plots are represented by a single curve for the displacement channels in the reactions of F- with CF₃Br and CF₃I. This implies that these reactions behave statistically, i.e., energy is randomized and distributed uniformly among the various degrees of freedom in the complex before dissociation.

We have made this type of measurement for several other S_N2 reactions. For the reactions of F- + CH₃X (X = Cl, Br, I)[6] and the reactions of Cl- with CH₃Br and CD₃Br,[38] we found that the reactivity depends only on translational energy and not on internal energy. More specifically, vibrational excitation does not affect the reactivity. This shows that, for these reactions of halide ions with monohalogenated methanes, vibrational and translational energy have different influences on the reactivity and that the reactions cannot be described by statistical theories.

We have also studied the S_N2 identity reaction of Cl- with ClCH₂CN.[41] As in the present case, differing kinetic energy and temperature dependences were found. Due to the low vapor pressure of the ClCH₂CN, the reaction could not be studied over a wide enough energy range to conduct the total energy test; i.e., the rate constants could not be compared at the same total energy but at different temperatures of the ClCH₂CN. However, RRKM modeling of this system was performed, and the RRKM calculations adequately predicted both the temperature and kinetic energy dependences, indicating that this reaction too behaves statistically.

Thus, we have found that the reactions involving monohalogenated methanes behave nonstatistically and all others we have studied behave statistically. The reason for this may be related to an additional observation: all of the reactions which behave statistically include at least a small contribution from an association pathway. For association to occur, the lifetime of the complex leading to association must be relatively long, on the order of the time between collisions with the helium buffer, or 10^{-7} s. In contrast, no association is seen for the reactions involving monohalogenated methanes, and the lifetimes for these complexes are estimated by theory to be very short, i.e., on the order of 10^{-12}–10^{-11} s.[5] Thus, in the statistical reactions there is a complex which has ample time for the energy to redistribute among all the degrees of freedom, and in the nonstatistical reactions there is not. This model is complicated by the possibility that different complexes lead to association and displacement. If different complexes are involved, it is possible that the lifetimes of these complexes do not differ by orders of magnitude, i.e., the complex for displacement may also be relatively long lived. Despite this complication, there appears to be a correlation between statistical behavior and the presence of an association component. This "association clock" might provide a useful indicator as to when a displacement reaction may be expected to behave statistically.

Conclusions

The result that the bimolecular displacement channels are not affected by pressure despite a large contribution by association to the overall reactivity indicates that these two channels do not

compete. This suggests the possibility that two different intermediate complexes are involved, one leading to displacement and the other to association.

The rate constants for association are more strongly reduced by the effects of increasing CF_3X internal energy than by those of increasing collision translational energy, a trend consistent with the predictions of ion–molecule association theory.[20-22]

The displacement reactions of F^- with CF_3Br and CF_3I are found to behave statistically. This conclusion is based on the observation that average total energy, regardless of the relative contributions from translational and internal energy, determines the reaction rate for displacement.

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